

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 USC 371

International Application No.: PCT/FI99/00741  
International Filing Date: September 13, 1999  
Priority Date Claimed: September 11, 1998  
Title of Invention: METHOD FOR GROWING OXIDE THIN FILMS CONTAINING BARIUM AND STRONTIUM  
Applicant(s) for DO/EO/US: Markku Leskela, Mikko Ritala, Timo Hatanpaa, Timo Hanninen, and Marko Vehkamaki

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. (X) This is a **FIRST** submission of items concerning a filing under 35 USC 371.
2. () This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 USC 371.
3. (X) This express request to begin national examination procedures (35 USC 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 USC 371(b) and PCT Articles 22 and 39(1).
4. (X) A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. (X) A copy of the International Application as filed (35 USC 371(c)(2))

  - a) () is transmitted herewith (required only if not transmitted by the International Bureau).
  - b) (X) has been transmitted by the International Bureau.
  - c) () is not required, as the application was filed in the United States Receiving Office (RO/US).
6. (X) Amendments to the claims of the International Application under PCT Article 19 (35 USC 371(c)(3))

  - a) () are transmitted herewith (required only if not transmitted by the International Bureau).
  - b) () have been transmitted by the International Bureau.
  - c) () have not been made; however, the time limit for making such amendments has NOT expired.
  - d) ☒ have not been made and will not be made.
7. (X) A copy of the International Preliminary Examination Report with any annexes thereto, such as any amendments made under PCT Article 34.

Items below concern other documents or information included:

8. (X) An Information Disclosure Statement under 37 CFR 1.97 and 1.98 and PTO Form 1449 with 5 references.
9. (X) International Search Report 3 pages.
10. (X) A FIRST preliminary amendment.

09/787062

Date: March 12, 2001

Page 2

11. (X) International Application as published.
12. (X) PCT request form.
13. (X) A return prepaid postcard.
14. (X) The following fees are submitted:

## FEES

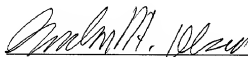
BASIC FEE				\$860
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total Claims	27 - 20 =	7 ×	\$18	\$126
Independent Claims	2 - 3 =	0 ×	\$80	\$0
Multiple dependent claims(s) (if applicable)			\$270	\$0
TOTAL OF ABOVE CALCULATIONS			\$986	
TOTAL NATIONAL FEE				\$986

15. (X) The fee for later submission of the signed oath or declaration set forth in 37 CFR 1.492(e) will be paid upon submission of the declaration.
16. (X) A check in the amount of \$986 to cover the above fees is enclosed.
17. (X) The Commissioner is hereby authorized to charge only those additional fees which may be required, now or in the future, to avoid abandonment of the application, or credit any overpayment to Deposit Account No. 11-1410. A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

KNOBBE, MARTENS, OLSON & BEAR, LLP  
620 Newport Center Drive  
Sixteenth Floor  
Newport Beach, CA 92660

  
Signature

Gordon H. Olson  
Printed Name

20,319  
Registration Number

09/787062

JG08 Rec'd PCT/PTO 12 MAR 2001

SEPP9.001APC

PATENT

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	:	Leskela et al.	)	Group Art Unit Unknown
			)	
Intl. Appl. No.	:	PCT/FI99/00741	)	
			)	
Intl. Filed	:	September 13, 1999	)	
			)	
For	:	METHOD FOR GROWING	)	
		OXIDE THIN FILMS	)	
		CONTAINING BARIUM AND	)	
		STRONTIUM	)	
			)	
Examiner	:	Unknown	)	

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
Washington, D.C. 20231

Dear Sir:

Preliminary to examination on the merits, please amend the above-captioned U.S. national phase application as follows:

IN THE SPECIFICATION:

On page 1 of the Specification, after the Title of the Invention ending on line 1 and before the sentence on line 4 which begins, "The present invention..." please insert: --This is the U.S. national phase under 35 U.S.C. § 371 of International Application PCT/FI99/00741, filed September 13, 1999.--

IN THE CLAIMS:**Please amend the claims as follows:**

1. (Amended) A method for growing oxide thin films on a substrate in a reactor, comprising producing the films by the Atomic Layer Epitaxy (ALE) process by feeding pulses of precursor compounds into the reactor, wherein the precursor compounds comprise:

at least one cyclopentadienyl compound of strontium and/or barium;

at least one volatile titanium compound; and  
a reactive oxygen precursor.

2. (Amended) The method according to Claim 1, wherein the oxide thin film is dielectric.

3. (Amended) The method according to Claim 1, wherein said method comprises 1-10 growth cycles in succession, wherein one growth cycle comprises:

feeding of a Ba compound, a Sr compound or a volatile titanium compound;  
an inert purge;  
feeding a reactive oxygen precursor; and  
a second inert purge.

4. (Amended) The method according to Claim 1, wherein the ratio of the at least one cyclopentadienyl compound of strontium and/or barium and the at least one volatile titanium compound is 0.8-1.2.

5. (Amended) The method according to Claim 1, wherein the volatile titanium compound is selected from the group consisting of a titanium halide, a titanium alkoxide, titanium nitrate ( $\text{Ti}(\text{NO}_3)_4$ ), an alkylamino complex of titanium, a cyclopentadienyl complex of titanium, a silylamido complex of titanium, titanium dialkyldithiocarbamate, and a titanium- $\beta$ -diketonate.

6. (Amended) The method according to Claim 1, wherein the substrate is selected from the group consisting of a platinum (Pt),  $\text{RuO}_2$ ,  $\text{IrO}_2$ ,  $\text{SrRuO}_3$ ,  $\text{LaSrCoO}_3$ ,  $\text{IrO}_2/\text{Ir}$ ,  $\text{RuO}_2/\text{Pt}$ , silica ( $\text{SiO}_2$ ), silicon nitride and a silicon surface.

7. (Amended) The method according to Claim 1, wherein the reactive oxygen precursor is selected from the group consisting of oxygen ( $\text{O}_2$ ), water vapor, hydrogen peroxide, an aqueous solution of hydrogen peroxide, ozone, and a combination thereof.

8. (Amended) The method according to Claim 1, wherein the at least one cyclopentadienyl compound of strontium and/or barium is  $\text{M}(\text{Cp})_2$  or  $\text{M}(\text{Cp})_2\text{L}_m$ , where

- M is Sr or Ba,
- Cp is a fused or single cyclopentadienyl group of the form  $\text{C}_5\text{R}_m\text{H}_{5-m}$ , where
- m is an integer 0-5 and
- R is a hydrocarbon group, wherein the m hydrocarbon groups are either the same or different,

- the Cp groups are either the same or different,
- $L_n$  is a neutral adduct ligand which binds to the metal by one or several of the atoms in said neutral adduct ligand.

9. (Amended) The method according to Claim 1, wherein

- the at least one cyclopentadienyl compound of strontium and/or barium is  $M(Cp)X$  or  $M(Cp)XL_n$ , where
- M is Sr or Ba,
- Cp is a fused or single cyclopentadienyl group  $C_5R_mH_{5-m}$ , where
- m is an integer 0-5 and
- R is a hydrocarbon group, wherein the m R's are either the same or different,
- X is a ligand having a valence of -1, wherein X is not a cyclopentadienyl group and
- L is a neutral adduct ligand which binds to the metal by one or several of the atoms making up said neutral adduct ligand.

10. (Amended) The method according to Claim 9, wherein the cyclopentadienyl group is selected from the group consisting of cyclopentadienyl, pentamethylcyclopentadienyl, triisopropylcyclopentadienyl, indenyl, and fluorenyl.

11. (Amended) The method according to Claim 8, wherein the two Cp groups are joined by a bridge.

12. (Amended) The method according to Claim 11, wherein the bridge between the two Cp groups is a substituted or unsubstituted  $C_1 - C_6$  carbon chain.

13. (Amended) The method according to Claim 12, wherein the carbon chain forming the bridge contains a heteroatom selected from the group consisting of silicon, nitrogen, phosphorus, selenium, and sulfur.

14. (Amended) The method according to Claim 9, wherein R is a substituted or unsubstituted, cyclic, linear or branched group selected from the group consisting of an alkyl, an alkenyl, an aryl, an arylalkyl, an alkoxy, a thio, an amino, a cyano and a silyl group.

15. (Amended) The method according to Claim 9, wherein the neutral adduct ligand L is selected from the group consisting of:

- (i) a hydrocarbon,
- (ii) an oxygen-containing hydrocarbon,

- (iii) a nitrogen-containing hydrocarbon,
  - (iv) a sulfur-containing hydrocarbon,
  - (v) a phosphorus-containing hydrocarbon,
  - (vi) an arsenic-containing hydrocarbon,
  - (vii) a selenium-containing hydrocarbon,
  - (viii) a tellurium-containing hydrocarbon,
- and a combination thereof.

16. (Amended) The method according to Claim 9, wherein L is selected from the group consisting of:

- (a) an amine or polyamine,
- (b) a bipyridine,
- (c) a ligand depicted by the formula



, where G is -O-, -S-, or -NR<sup>1</sup>-, where R<sup>1</sup> is hydrogen or a substituted or unsubstituted, cyclic, linear or branched group selected from the group consisting of an alkyl, an alkenyl, an aryl, an alkylaryl, an arylalkyl, an alkoxy, a thio, a cyano and a silyl group, and wherein each carbon atom of the ring according the formula has an R<sup>1</sup>-like substituent, wherein the substituents are either [mutually] the same or different,

- (d) ether, and
- (e) thioether.

17. (Amended) The method according to Claim 9, wherein L is selected from the group consisting of an ether, a polyether, an amine, a polyamine, bipyridine and tetrahydrofuran.

18. (Amended) The method according to Claim 9, wherein X is selected from the group consisting of a  $\beta$ -ketonate, a corresponding sulfur or nitrogen compound, an alkyl, a halide, an amide, an alkoxide, a carboxylate and a Schiff base.

19. (Amended) The method according to Claim 1, wherein the producing of the film takes place at 250-300°C.

**Please add the following new claims:**

20. (New) The method according to Claim 3, wherein said method comprises 1-2 growth cycles.
21. (New) The method according to Claim 9, wherein the cyclopentadienyl group is selected from the group consisting of cyclopentadienyl, pentamethylcyclopentadienyl, triisopropylcyclopentadienyl, indenyl, and fluorenyl.
22. (New) The method according to Claim 9, wherein R is a substituted or unsubstituted, cyclic, linear or branched group selected from the group consisting of an alkyl, an alkenyl, an aryl, an alkylaryl, an arylalkyl, an alkoxy, a thio, an amino, a cyano and a silyl group.
23. (New) The method according to Claim 9, wherein the neutral adduct ligand L is selected from the group consisting of:
- (i) a hydrocarbon,
  - (ii) an oxygen-containing hydrocarbon,
  - (iii) a nitrogen-containing hydrocarbon,
  - (iv) a sulfur-containing hydrocarbon,
  - (v) a phosphorus-containing hydrocarbon,
  - (vi) an arsenic-containing hydrocarbon,
  - (vii) a selenium-containing hydrocarbon,
  - (viii) a tellurium-containing hydrocarbon,
- and a combination thereof.
24. (New) The method according to Claim 9, wherein L is selected from the group consisting of:
- (a) an amine or polyamine,
  - (b) a bipyridine,
  - (c) a ligand depicted by the formula



, where G is -O-, -S-, or -NR<sup>1</sup>-, where R<sup>1</sup> is hydrogen or a substituted or unsubstituted, cyclic, linear or branched group selected from the group consisting

of an alkyl, an alkenyl, an aryl, an alkylaryl, an arylalkyl, an alkoxy, a thio, a cyano and a silyl group, and wherein each carbon atom of the ring according to the formula has an R<sup>1</sup>-like substituent, wherein the substituents are either the same or different,

(d) ether, and

(e) thioether.

25. (New) The method according to Claim 19, further comprising postannealing said film at a temperature higher than a temperature at which the producing of the film takes place.

26. (New) The method according to Claim 25, wherein postannealing said film takes place at 500°C.

27. (New) A method for growing oxide thin films on a substrate in a reactor, comprising producing the films by the Atomic Layer Epitaxy (ALE) process by feeding pulses of precursor compounds into the reactor, wherein the precursor compounds comprise:

at least one cyclopentadienyl compound of strontium and/or barium; and  
a reactive oxygen precursor.



Intl. Appl. No. : PCT/FI99/00741  
Intl. Filed : September 13, 1999

REMARKS

Claims 1-19 have been amended to more precisely claim the invention according to conventional practice before the United States Patent and Trademark Office. Claims 20-27 have been added. Claims 1-27 are presented for examination. New Claims 20-25 claim matter originally in Claims 3, 10, 14, 15, 16, and 19 respectively. No new matter is being added.

The changes to the claims are shown on a separate set of pages attached hereto entitled VERSION WITH MARKING TO SHOW CHANGES MADE, which follows the signature page of this Preliminary Amendment.

Should there be any questions concerning this application, the Examiner is respectfully requested to contact the undersigned attorney at the telephone number appearing below.

Respectfully submitted,

KNOBBE, MARTENS, OLSON & BEAR, LLP

Dated: 3/12/01

By: 

Gordon H. Olson  
Registration No. 20,319  
Attorney of Record  
620 Newport Center Drive  
Sixteenth Floor  
Newport Beach, CA 92660

**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

1. (Amended) A method for growing oxide thin films on a substrate in a reactor, **[characterized in that]** comprising producing the films [are produced] by the Atomic Layer Epitaxy (ALE) process by **[using as the]** feeding pulses of precursor compounds into the reactor, wherein the precursor compounds [are] comprise:

at least one cyclopentadienyl compound[s] of strontium and/or barium[.];**[together with]**

at least one [or more] volatile titanium compound[s]; and  
cycles in succession, wherein one growth cycle **[being made up of the]** comprises:  
feeding of a reactive oxygen precursor.

2. (Amended) The method according to Claim 1, **[characterized in that]** wherein the oxide thin film **[to be grown]** is dielectric.

3. (Amended) The method according to Claim 1 **[or 2, characterized in that there are]**, wherein said method comprises 1-10 [, preferably 1-2, similar] growth Ba compound, a Sr compound or a volatile titanium compound;

an inert purge;

**[the]** feeding **[of]** a reactive oxygen precursor **[for oxygen]**; and

a second inert purge.

4. (Amended) The method according to **[any of]** Claim[s] 1 [- 3], **[characterized in that]** wherein the [cycle] ratio of the [alkaline earth metal] at least one cyclopentadienyl compound of strontium and/or barium and the at least one volatile titanium compound is 0.8-1.2.

5. (Amended) The method according to **[any of]** Claim[s] 1 [- 4, **characterized in that**] , wherein the volatile titanium compound is selected from the group consisting of a titanium halide, a titanium alkoxide, titanium nitrate ( $\text{Ti}(\text{NO}_3)_4$ ), an alkylamino complex of titanium, a cyclopentadienyl complex of titanium, a silylamido complex of titanium, titanium dialkylthiocarbamate, **[or]** and a titanium- $\beta$ -diketonate.

6. (Amended) The method according to **[any of the preceding claims]** Claim 1, **[characterized in that the film growth]** wherein the substrate is selected from the group consisting of a platinum (Pt),  $\text{RuO}_2$ ,  $\text{IrO}_2$ ,  $\text{SrRuO}_3$ ,  $\text{LaSrCoO}_3$ ,  $\text{IrO}_2/\text{Ir}$ ,  $\text{RuO}_2/\text{Pt}$ , silica ( $\text{SiO}_2$ ), silicon nitride **[or]** and a silicon surface.

7. (Amended) The method according to **[any of the preceding claims]** Claim 1, [characterized in that] wherein the reactive oxygen precursor [used] is selected from the group consisting of oxygen (O<sub>2</sub>), water vapor, hydrogen peroxide [or] , an aqueous solution of hydrogen peroxide, [and/or] ozone, and a combination thereof.

8. (Amended) The method according to **[any of the preceding claims, characterized in that]** Claim 1, wherein the [formula of the precursor] at least one cyclopentadienyl compound of strontium and/or barium is M(Cp)<sub>2</sub> or M(Cp)<sub>2</sub>L<sub>n</sub>, where M is Sr or Ba,

Cp is a fused or single cyclopentadienyl group of the form **[Cp']C<sub>5</sub>R<sub>m</sub>H<sub>5-m</sub>**, where m is an integer 0-5 and

R is a hydrocarbon group, wherein the m hydrocarbon groups [being mutually] are either the same or different,

the Cp groups are either the same or different,

L<sub>n</sub> is a neutral adduct ligand which binds to the metal by one or several of **[its] the atoms in said neutral adduct ligand.**

9. (Amended) The method according to **[any of]** Claim[s] 1 [- 7, **characterized in that], wherein**

- the **[precursor for Sr and/or Ba]** at least one cyclopentadienyl compound of strontium and/or barium is [of the form] M(Cp)X or M(Cp)XL<sub>n</sub>, where
- M is Sr or Ba,
- Cp is a fused or single cyclopentadienyl group **[Cp']C<sub>5</sub>R<sub>m</sub>H<sub>5-m</sub>**, where
- m is an integer 0-5 and
- R is a hydrocarbon group, wherein the m R's are [being mutually] either the same or different,
- X is a ligand, **other than Cp,** having a valence of -1, wherein X is not a cyclopentadienyl group and
- L is a neutral adduct ligand which binds to the metal by one or several of **[its] the atoms making up said neutral adduct ligand.**

10. (Amended) The method according to Claim 8 **[or 9, characterized in that] , wherein the cyclopentadienyl group is selected from the group consisting of cyclopentadienyl, pentamethylcyclopentadienyl, triisopropylcyclopentadienyl, indenyl, [or] and fluorenyl.**

11. (Amended) The method according to Claim 8 [or 9, **characterized in that**] ,  
wherein the two Cp groups are [**contained in the same molecule**] joined by a bridge.

12. (Amended) The method according to Claim 11, [**characterized in that**]  
wherein the bridge between the two Cp groups is [**made up of**] a substituted or unsubstituted C<sub>1</sub>  
- C<sub>6</sub> carbon chain.

13. (Amended) The method according to Claim 12, [**characterized in that**]  
wherein the carbon chain forming the bridge contains a heteroatom[, **which is**] selected from the  
group consisting of silicon, nitrogen, phosphorus, selenium, [**or**] and sulfur.

14. (Amended) The method according to Claim 8 [or 9], [**characterized in that**]  
wherein R is a substituted or unsubstituted, cyclic, linear or branched group selected from the  
group consisting of an alkyl, an alkenyl, an aryl, an alkylaryl, an arylalkyl, an alkoxy, a thio, an  
amino, a cyano [**or**] and a silyl group.

15. (Amended) The method according to Claim 8 [or 9, **characterized in that**],  
wherein the neutral adduct ligand L is selected from the group consisting of:

- a hydrocarbon,
- an oxygen-containing hydrocarbon,
- a nitrogen-containing hydrocarbon,
- a sulfur-containing hydrocarbon,
- a phosphorus-containing hydrocarbon,
- an arsenic-containing hydrocarbon,
- a selenium-containing hydrocarbon, [**and/or**]
- a tellurium-containing hydrocarbon,
- and a combination thereof.

16. (Amended) The method according to Claim 8 [or 9, **characterized in that**],  
wherein L is selected from the group consisting of:

- (a) an amine or polyamine,
- (b) a bipyridine,
- (c) a ligand depicted by the formula



[in which formula] , where G is -O-, -S-, or -NR<sup>1</sup>-, where R<sup>1</sup> is hydrogen or a substituted or unsubstituted, cyclic, linear or branched[,] group selected from the group consisting of an alkyl, an alkenyl, an aryl, an alkylaryl, an arylalkyl, an alkoxy, a thio, a cyano [or] and a silyl group, and wherein each carbon atom of the ring according to the formula [there is] has an R<sup>1</sup>-like substituent, wherein the substituents [which] are either [mutually] the same or different,

(d) ether, [or] and

(e) thioether.

17. (Amended) The method according to Claim 8 [or 9], wherein L is selected from the group consisting of an ether, a polyether, an amine, a polyamine, bipyridine [or] and tetrahydrofuran.

18. (Amended) The method according to Claim 9, wherein [characterized in that] X is selected from the group consisting of a  $\beta$ -ketonate, [or] a corresponding sulfur or nitrogen compound, an alkyl, a halide, an amide, an alkoxide, a carboxylate [or] and a Schiff base.

19. (Amended) The method according to [any of the preceding claims] Claim 1, [characterized in that] wherein the [growth] producing of the film takes place at 250-300°C[, and the postannealing carried out after the growth takes place at a temperature higher than the deposition temperature, preferably at 500°C].

20. (New) The method according to Claim 3, wherein said method comprises 1-2 growth cycles.

21. (New) The method according to Claim 9, wherein the cyclopentadienyl group is selected from the group consisting of cyclopentadienyl, pentamethylcyclopentadienyl, triisopropylcyclopentadienyl, indenyl, and fluorenyl.

22. (New) The method according to Claim 9, wherein R is a substituted or unsubstituted, cyclic, linear or branched group selected from the group consisting of an alkyl, an alkenyl, an aryl, an alkylaryl, an arylalkyl, an alkoxy, a thio, an amino, a cyano and a silyl group.

23. (New) The method according to Claim 9, wherein the neutral adduct ligand L is selected from the group consisting of:

- (i) a hydrocarbon,
  - (ii) an oxygen-containing hydrocarbon,
  - (iii) a nitrogen-containing hydrocarbon,
  - (iv) a sulfur-containing hydrocarbon,
  - (v) a phosphorus-containing hydrocarbon,
  - (vi) an arsenic-containing hydrocarbon,
  - (vii) a selenium-containing hydrocarbon,
  - (viii) a tellurium-containing hydrocarbon,
- and a combination thereof.

24. (New) The method according to Claim 9, wherein L is selected from the group consisting of:

- (a) an amine or polyamine,
- (b) a bipyridine,
- (c) a ligand depicted by the formula



, where G is -O-, -S-, or -NR<sup>1</sup>-, where R<sup>1</sup> is hydrogen or a substituted or unsubstituted, cyclic, linear or branched group selected from the group consisting of an alkyl, an alkenyl, an aryl, an alkylaryl, an arylalkyl, an alkoxy, a thio, a cyano and a silyl group, and wherein each carbon atom of the ring according the formula has an R<sup>1</sup>-like substituent, wherein the substituents are either the same or different,

- (d) ether, and
- (e) thioether.

**Intl. Appl. No.** : **PCT/FI99/00741**  
**Intl. Filed** : **September 13, 1999**

25. (New) The method according to Claim 19, further comprising postannealing said film at a temperature higher than a temperature at which the producing of the film takes place.

26. (New) The method according to Claim 24, wherein postannealing said film takes place at 500°C.

27. (New) A method for growing oxide thin films on a substrate in a reactor, comprising producing the films by the Atomic Layer Epitaxy (ALE) process by feeding pulses of precursor compounds into the reactor, wherein the precursor compounds comprise:  
at least one cyclopentadienyl compound of strontium and/or barium; and  
a reactive oxygen precursor.

H:\DOCS\JWK\JWK-3904.DOC  
030801

**Method for growing oxide thin films containing barium and strontium**

5 The present invention relates to high permittivity oxide films and superconductive materials which contain barium and/or strontium. A particular object of the invention is the method according to the preamble of Claim 1 for producing such films and materials.

10 Dielectric thin films having high dielectric constants (permittivities) are required in many sub-areas of microelectronics and optoelectronics. In particular, the continual decrease in the size of microelectronics components has increased the need for the use of such dielectric films. For example, the capacitance of DRAM (Dynamic Random Access Memory) capacitors must remain nearly constant while their size decreases rapidly, and thus it is necessary to replace the previously used  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  with materials which have higher permittivities than these. In optoelectronics, dielectric films having high  
15 permittivities can be exploited in, for example, electroluminescence displays, in which the operating voltage of the displays can be reduced by means thereof. Some dielectric materials having high permittivities, e.g.  $\text{BaTiO}_3$ , are also ferroelectric materials at normal temperatures, a factor which further extends their potential uses, for example, to NVRAM (Nonvolatile Random Access Memory) and various microelectromechanical applications.

20 In addition to high permittivities, these dielectric thin films are required to have, among other things, low leakage current densities and high dielectric breakdown fields. The achievement of both of these properties presupposes a dense and flawless film structure. Of course, the properties of the films must be stable in the conditions of use. Furthermore, in particular in microelectronics applications, the conformality of the films, i.e. their capacity  
25 to cover surfaces of complicated shapes with a film of a uniform thickness is important, because in the manufacture of microelectronics components it is necessary to deposit films even in deep trenches and holes.

30 Oxide thin films containing barium and strontium are widely used and researched dielectric films having high permittivities. Important oxide thin films containing barium and strontium include, for example,  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  ( $x$  is 0-1). In addition to these there can be mentioned high-temperature superconductors, e.g.  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $x$  is 0-1),  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$  and  $\text{Ti}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$ , and dielectric materials lattice-

09787062-000001



matched therewith,  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{Sr}_2\text{AlTaO}_6$  (D.L. Schulz and T.J. Marks, *Advanced Materials* 6 (1994) 719). In all of the above-mentioned formulae,  $n$  is 1-3 and  $\delta$  is 0-1. Other oxide films containing barium and strontium include various niobates  $(\text{Sr},\text{Ba})\text{Nb}_2\text{O}_6$  and  $(\text{Pb},\text{Ba})\text{Nb}_2\text{O}_6$  (L.M. Shepard, *Ceramic Bulletin* 71 (1992) 85). These films have been  
 5 manufactured by many different methods, such as the sol-gel method, various physical vapor deposition methods (PVD) (e.g. vaporization, sputtering, laser ablation) and chemical vapor deposition methods (CVD).

Films manufactured by the sol-gel method, by various physical vapor deposition methods  
 10 (PVD) (e.g. vaporization, sputtering, laser ablation) and by chemical vapor deposition methods (CVD) are of a high quality. Instead, the manufacture of a film of uniform quality and thickness when the surface structure of the piece is complicated will not succeed. Only by the CVD method is it possible to deposit conformal films in deep trenches and holes (S.M. Bilodeau, *Solid State Technology*, July (1997) 235). Even in the CVD method, high  
 15 conformality is attained only when the rate of film growth is determined by the rate of the surface reaction and not by the diffusion of the precursors on the film surface. This is achieved when the surface reaction is slower than the diffusion of the precursors on the film surface. The surface reaction is slow at low temperatures, but in such a case the other properties of the film will, however, often remain poor, which is due to both the poor  
 20 crystallinity of the film and to difficulties in the control of its composition (C.S. Kang et al., *Japanese Journal of Applied Physics*, Part 1 36 (1997) 6946; M. Kiyotoshi and K. Eguchi, *Electrochemical Society Proceedings* 97-25 (1997) 1063).

Atomic Layer Epitaxy (ALE), which is also known as Atomic Layer Chemical Vapor  
 25 Deposition (ALCVD) or Atomic Layer Deposition (ALD), is a known method for the deposition of thin films (US patent publication 4.085.430). In this method, the thin film is deposited by means of alternate saturating surface reactions. These reactions are implemented by feeding gaseous or vaporized precursors into the reactor alternately and by purging the reactor with an inert gas between the precursor pulses (T. Suntola, *Thin Solid*  
 30 *Films* 215 (1992) 84; Niinistö et al., *Materials Science and Engineering B* 41 (1996) 23). In addition, ALE can be used for depositing layers of uniform thickness even on large surfaces, and the control of the thickness and composition by means of the number of reaction cycles is precise and simple.

The ALE method has previously been used for making  $\text{TiO}_2$  films (Ritala et al., Thin Solid Films 225 (1993) 288, Chemistry of Materials 5 (1993) 1174 and 6 (1994) 556), but so far it has not been possible to manufacture the barium- and strontium-containing oxide thin films which are the object of the present invention by the ALE method in a self-controlling manner. Attempts at self-controlling deposition of superconductive films have also failed. The most important reason for not manufacturing the above-mentioned compounds is the lack of suitable precursors for Ba and Sr. Few of the compounds of the said elements are volatile, and so the precursors used in both CVD and ALE have as a rule been of one compound type, i.e.  $\beta$ -diketonates (W.A. Wojtcak et al., Advances in Organometallic Chemistry 40 (1996) 215, Tiitta and Niinistö, Chemical Vapor Deposition 3 (1997) 167). The problem with the  $\beta$ -diketonates of Ba and Sr is that they do not react with the oxygen sources,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$  and  $\text{O}_2$ , most typically used in the ALE method, at temperatures at which they would not decompose thermally. Iodides of the said metals have also been used in the CVD method (P. Mårtensson and A. Hårsta, Journal of Crystal Growth 156 (1995) 67), but in this case it is necessary to use temperatures which are too high for most applications.

EP application publication No. 344 352 describes a method for making laminated superconductors by an epitaxy method. The ALE method is also mentioned. The application publication also lists suitable organometallic compounds which can be used as precursors in these methods. Barium cyclopentadienyl is also among them. However, in the publication a film has not been deposited by specifically the ALE method and by using specifically barium cyclopentadienyl as the precursor. Furthermore, the EP publication does not provide preferred conditions for the film growth, since it does not state how or in what conditions cyclopentadienyl compounds should be used, how oxygen is introduced into the oxides or what advantages would follow specifically from the use of barium cyclopentadienyl as the precursor in any of the alternative epitaxy methods described in the publication.

It is an object of the present invention to eliminate the deficiencies described above and to provide a novel method for the manufacture of thin films and superconductive materials which contain barium and strontium.

The invention is based on the observation that the barium and strontium compounds

according to the invention are sufficiently stable in a gas phase, and consequently these compounds can be used as precursors in the ALE technique, and thus oxide thin films which contain barium and strontium can be deposited in a controlled manner. The cyclopentadienyl compounds of barium and strontium are such vaporizable compounds. In the deposition of film, the said barium and strontium compounds are used as precursors in a method according to the ALE principle together with a reactive oxygen precursor and a volatile titanium compound.

More specifically, the method according to the invention is characterized by what is stated in the characterizing part of Claim 1.

The invention will be discussed below with the help of the accompanying drawings.

Figure 1 depicts the composition of a multi-component film as a function of the cycle ratio of the various components.

Figure 2 depicts an X-ray diffraction analysis of the thin film.

Figure 3 depicts the permittivities of films deposited at 325 °C, as a function of the cycle ratio, as measured from the structure ITO/SrTiO<sub>3</sub>/Al, where ITO is indium-tin oxide.

In the technical solution according to the invention, oxide thin films are deposited in an ALE reactor at a temperature of 100-700 °C, preferably 150-400 °C. Either sheet-form (such as glass or silicon wafer) or pulverous materials can be used as the substrate. According to the ALE method, a cyclopentadienyl compound containing an earth-alkali metal is vaporized, whereafter the reactor is purged with an inert gas, the oxygen precursor is fed into the reactor, and the reactor is purged for a second time with an inert gas. All of these steps together constitute one deposition cycle. The deposition cycle is repeated until the film is of the desired thickness. A multi-component film is obtained by changing the precursor.

In connection with the present invention, cyclopentadienyl compounds of barium or strontium are used as precursors. By these compounds is meant any compound according to Formulae I-IV.

	$M(Cp)_2$	(I)
	$M(Cp)_2L_n$	(II)
	$M(Cp)X$	(III)
5	$M(Cp)XL_n$	(IV),

in which formulae

M is Ba or Sr;

10

Cp is a cyclopentadienyl group, the Cp groups present in Formulae I and II being mutually the same or different;

X is a ligand other than Cp, with the valency of -1;

15

$L_n$  is a neutral adduct ligand which binds to a metal by either one or several of its atoms, and n depicts the number of the ligands being bound.

20

In Formulae I-IV the cyclopentadienyl groups may also be in the same molecule. In this case the bridge between two Cp groups is made up of a substituted or unsubstituted  $C_1-C_6$  chain, which may contain a heteroatom which is Si, N, P, Se or S.

Ligand X is preferably  $\beta$ -diketonate or a corresponding sulfur or nitrogen compound, halide, amide, alkoxide, carboxylate or Schiff base.

25

L is preferably

30

- (i) a hydrocarbon,
- (ii) an oxygen-containing hydrocarbon,
- (iii) a nitrogen-containing hydrocarbon,
- (iv) a sulfur-containing hydrocarbon,
- (v) a phosphorus-containing hydrocarbon,
- (vi) an arsenic-containing hydrocarbon,
- (vii) a selenium-containing hydrocarbon, and/or
- (viii) a tellurium-containing hydrocarbon.

Most preferably L is

- (a) an amine or a polyamine,
- (b) a bipyridine,
- (c) a ligand depicted by the formula



(V)

in which formula G is -O-, -S-, or -NR<sup>1</sup>-, where R<sup>1</sup> is hydrogen or a substituted or unsubstituted, cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, cyano or silyl group. The cyclic or aromatic ring of R<sup>1</sup> may contain a heteroatom. The ligand depicted by Formula V may also have either hydrogen or a substituent like R<sup>1</sup> attached to the carbon atoms,

- (d) ether or thioether.

The cyclopentadienyl group (Cp) in Formulae I-IV is of the form



where m is an integer of 0-5,

Cp' is a fused or individual cyclopentadienyl, and

R is a hydrocarbon radical containing 1-20 carbon atoms, preferably a C<sub>1</sub>-C<sub>6</sub> hydrocarbon. The R's may be mutually the same or different. R may be a substituted or unsubstituted, cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, amino, cyano or silyl group. The cyclic or aromatic ring of the substituent may contain a heteroatom. Methyl, ethyl, propyl and isopropyl groups can be mentioned as examples of the substituents.

Preferably there is used an organometallic complex according to Formula II, where Cp is cyclopentadienyl, indenyl or fluorenyl. As the neutral adduct ligand L (Formulae II and IV) there are used, for example, ethers, amines or solvent molecules (e.g. tetrahydrofuran) which bind to the metal by one atom. Polyethers and polyamines can be mentioned as examples of suitable ligands which bind to the metal by several of their atoms.

According to the invention, the precursor used for the oxide thin film is especially preferably a THF adduct of bis(pentamethylcyclopentadienyl) or bis(triisopropylcyclopentadienyl) of barium or strontium.

5

According to the first preferred embodiment of the invention, the cyclopentadienyl compounds of barium and strontium are used together with a volatile titanium compound (e.g. a halide, alkoxide, cyclopentadienyl, alkylamide) and a reactive oxygen precursor (e.g.  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}_2$ ), in which case  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$  films can be grown by the ALE method at low deposition temperatures ( $325^\circ\text{C}$ ). The said precursors can also be exploited in ALE deposition of other oxide thin films containing barium and/or strontium.

10

Below there are listed titanium compounds which have vapor pressures sufficient at a temperature lower than the temperature of the deposition substrate, and which are thus suitable for use in the method according to the present invention. Thus, preferably one or more of the following compounds are used as the volatile titanium compound:

15

- titanium halides, for example  $\text{TiCl}_4$ ,  $\text{TiCl}_3$ ,  $\text{TiBr}_3$ ,  $\text{TiI}_4$ ,  $\text{TiI}_3$ ,
- titanium alkoxides, for example  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Ti}(\text{O}^i\text{Pr})_4$ ,  $\text{Ti}(\text{O}^n\text{Bu})_4$  and titanium(IV)-ethylhexoxide,
- titanium nitrate ( $\text{Ti}(\text{NO}_3)_4$ ),
- alkylamino complexes of titanium, for example tetrakis(diethylamino)titanium, tetrakis(dimethylamino)titanium, tetrakis(ethylmethylamino)titanium, tetrakis(isopropylmethylamino)titanium, bis(cyclopentadienyl)bis(dimethylamino)titanium, tris(dimethylamino)(N,N,N'-trimethylethyldiamino)titanium, and tert-butyltris(dimethylamino)titanium; further examples of applicable compounds are described in US patent No. 5,659,057,
- cyclopentadienyl complexes of titanium, for example  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2$ ,  $\text{Ti}(\eta^5\text{-C}_5\text{H}_5)(\eta^7\text{-C}_7\text{H}_7)$ ,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiR}_2$ , where R = alkyl (e.g.  $\text{CH}_3$ ), benzyl ( $\text{C}_6\text{H}_5$ ) or carbonyl, bis(t-butylcyclopentadienyl)titanium dichloride, bis(pentamethylcyclopentadienyl) titanium dichloride, and  $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ ,
- silylamido complexes of titanium, such as  $\text{Ti}\{\text{N}_4[\text{Si}(\text{CH}_3)_3]_4[\text{Si}(\text{CH}_3)_2]_2\}$ ; further examples of applicable compounds are described in US patent No. 5,603,988,
- titaniumdialkylidithiocarbamates, and
- titanium- $\beta$ -diketonates, for example di(i-propoxide)bis(2,2,6,6-tetramethyl-3,5-

20

25

30

heptanedionato)titanium, and tris(2,2,6,6,-tetramethyl-3,5-heptanedionato)-titanium(III).

Especially preferably, titanium tetraisopropoxide ( $\text{Ti}(\text{O}^i\text{C}_3\text{H}_7)_4$ ) is used.

The oxygen precursor may be any oxygen compound usable in the ALE technique. Preferable oxygen precursors include water, oxygen and hydrogen peroxide, and aqueous solutions of hydrogen peroxide. Ozone ( $\text{O}_3$ ) is an especially preferable oxygen precursor. It is known on the basis of the literature that, if ozone is used as the precursor for oxygen, a denser layer of material is obtained from the forming oxides, and thereby the permittivity of the oxide thin film can be improved.

One or more of the following compounds may also be used as the precursor for oxygen:

- oxides of nitrogen, such as  $\text{N}_2\text{O}$ ,  $\text{NO}$ , and  $\text{NO}_2$ ,
- halide-oxygen compounds, for example chlorine dioxide ( $\text{ClO}_2$ ) and perchloric acid ( $\text{HClO}_4$ ), the compatibility of these with earth-alkali metals being, however, limited,
- peracids ( $-\text{O}-\text{O}-\text{H}$ ), for example perbenzoic acid ( $\text{C}_6\text{H}_5\text{COOOH}$ ) and peracetic acid ( $\text{CH}_3\text{COOOH}$ ),
- alcohols, such as methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), and
- various radicals, for example oxygen radical ( $\text{O}^\cdot$ ) and hydroxyl radical ( $^\cdot\text{OH}$ ).

According to a second preferred embodiment, the ratio of the deposition cycles (e.g.  $\text{Ti}-\text{O}$ ,  $\text{Sr}-\text{O}$  and  $\text{Ba}-\text{O}$ ) producing the different binary oxides of multicomponent oxide films (e.g.  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ) is controlled. If, for example,  $\text{Sr}/\text{Ti}$  is 0.8-1.2, preferably approx. 1, a crystalline film is obtained (cf. Example 1). Thus the composition can be controlled simply and with precision. In order that the composition of the film should be uniform, the deposition cycles are carried out so that the different materials become mixed as completely as possible, i.e. there will be 1-10, preferably 1-2 similar cycles in succession.

According to a third preferred embodiment, the oxide film is grown at a lower temperature (250-300 °C), whereby an amorphous thin film is obtained. The structure of the film

becomes crystalline during postannealing. The postannealing is carried out at a temperature higher than the growth temperature, and its duration may vary. According to a preferred embodiment of the invention, the duration of the postannealing is 60 min, and it is carried out in an air stream at 500 °C.

5

Considerable advantages are gained with the help of the invention. Since according to the ALE method the film grows through saturating surface reactions, the growth is self-controlling, which in turn ensures excellent conformality. As is evident from the above, cyclopentadienyl compounds of strontium and barium can be used as vaporizing components within a wide temperature range, in which case the structure of the thin film made and its crystallinity can be effectively controlled by the selection of the reaction temperature and the metal mixing ratio and by a potential post-treatment. The present precursors are especially advantageous for use in the ALE technique also for the reason that they will not leave significant carbon or hydrogen residues in the final product. On the other hand, the dielectric constants of oxide thin films containing barium and strontium are very high, and thus the oxides of specifically barium and strontium are especially suitable as materials for dielectric thin films. Owing to their high dielectric constants they are especially suitable for memory circuits and for gate oxides. By the use of cyclopentadienyl compounds of barium together with a volatile titanium compound, a low-temperature growth process is achieved, which is important in most applications of dielectric films.

10

15

20

In the context of the present invention, by dielectric oxide thin film is meant a thin film having a high permittivity. The permittivity varies according to the thickness of the film so that the permittivity of a thinner film is lower. It can be noted as an example that for a film approx. 50 nm thick a high permittivity is approx. 50 or more, preferably approx. 100 or more.

25

Thin films according to the invention are preferably used as dielectric films of various electronics components. Films according to the invention are deposited, for example, on platinum (Pt), RuO<sub>2</sub>, IrO<sub>2</sub>, SrRuO<sub>3</sub>, LaSrCoO<sub>3</sub>, IrO<sub>2</sub>/Ir, RuO<sub>2</sub>/Pt, silica (SiO<sub>2</sub>), silicon nitride and silicon surfaces.

30

By means of the present invention it is possible to make, in addition to the above-mentioned thin films, also high-temperature superconductors mentioned in the preamble,



for example  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $x$  is 0-1),  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$  and  $\text{Ti}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{5+(2n-1)+\delta}$ , and dielectric materials lattice-matched therewith, such as  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , and  $\text{Sr}_2\text{AlTaO}_6$  (D. L. Schulz and T. J. Marks, *Advanced Materials* 6 (1994) 719).

- 5 Three examples are presented below in order to illustrate the invention.

### Example 1

- 10  $\text{SrTiO}_3$  films were grown in a flow-type F-120 ALE reactor (Mikrokemia Oy) at a temperature of 325 °C. The strontium precursor used was the THF adduct of bis(triisopropylcyclopentadienyl) strontium,  $\text{Sr}(\text{C}_5(\text{C}_3\text{H}_7)_2)_2\text{THFG}_p$ , in which  $p = 0-2$  and THF is tetrahydrofuran, and which was vaporized in the reactor by heating it to a temperature of 100 °C. The titanium precursor used was titanium tetraisopropoxide
- 15  $(\text{Ti}(\text{O}(\text{C}_3\text{H}_7)_4)_4)$ , which was vaporized in the reactor at a temperature of 40 °C. The oxygen source used was water, which was fed into the reactor from outside it. The growth of  $\text{TiO}_2$  from the said precursors has been described previously (Ritala et al., *Chemistry of Materials* 5 (1993) 1174).
- 20 The growth of  $\text{SrTiO}_3$  was implemented by using alternate Ti-O and Sr-O deposition cycles. The Ti-O cycle was made up of four steps: (i) an 0.6 s pulse of  $\text{Ti}(\text{O}(\text{C}_3\text{H}_7)_4)_4$ , an 0.5 s purge with inert nitrogen gas, (iii) an 0.6 pulse of  $\text{H}_2\text{O}$ , and (iv) an 0.5 s purge with nitrogen gas. Respectively, the composition of the Sr-O cycle was: (i) an 0.6 s pulse of  $\text{Sr}(\text{C}_5(\text{C}_3\text{H}_7)_2)_2\text{THFG}_p$ , (ii) an 0.5 s purge with nitrogen gas, (iii) an 0.5 s pulse of  $\text{H}_2\text{O}$ , and (iv)
- 25 an 0.5 s purge with nitrogen gas. The composition of the film was controlled by the ratio of the Ti-O and Sr-O cycles. The alternation of the Ti-O and Sr-O cycles was implemented so that there were at maximum two similar cycles in succession. For example, the cycle ratio  $\text{Ti-O/Sr-O} = 1:1$  was achieved by repeating the cycling formula  $q[(\text{Ti-O})(\text{Sr-O})]$  and the ratio  $\text{Ti-O/Sr-O} = 3:4$  by means of the formula  $q[(\text{Ti-O})(\text{Sr-O})(\text{Ti-O})(\text{Sr-O})(\text{Ti-O})(\text{Sr-O})(\text{Sr-O})]$ , in which formulae  $q$  indicates how many times the said cycling was repeated.
- 30 Thus  $q$  determines the thickness of the film.

When the films were grown at a temperature of 325 °C, their composition varied according to the cycle ratio (Figure 1). The linearity of the curve shown in the figure is an indication

that the composition can well be controlled by means of the cycle ratio. Films having Sr/Ti ratios close to 1 were, according to an X-ray diffraction analysis, crystalline SrTiO<sub>3</sub> (Figure 2). TOF-ERDA (Time-of-Flight Elastic Recoil and Detection Analysis) showed that the films contained carbon and hydrogen residues lower than 0.2 at.%, the other possible impurity residues being so low that they cannot be detected by the method concerned.

Figure 3 shows the effect of the post-treatment on the permittivity of the film. The permittivities of films without post-treatment are at maximum 118, but annealing in air at a temperature of 500 °C for 60 min increases permittivity significantly, the highest values being 180. The postannealing also increased the intensity of X-ray reflections, showing an improved film crystallinity.

### Example 2

The process according to Example 1 was repeated using a growth temperature of 250 °C. The films thus grown were amorphous, but they crystallized when they were heated in air at 500 °C for 60 min.

### Example 3

BaTiO<sub>3</sub> films were grown in the manner described in Example 1, but by using instead of Sr(C<sub>5</sub>(C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>H<sub>2</sub>)<sub>2</sub>THF<sub>p</sub>, a THF adduct of bis(pentamethylcyclopentadienyl)barium, Ba(C<sub>5</sub>(CH<sub>3</sub>)<sub>4</sub>)THF<sub>p</sub>, where x = 0-2. The deposition temperature was 250 °C. When a deposition cycle ratio of (Ti-O)/(Ba-O) = 6:5 was used, an amorphous film was obtained. When this film was heated in air at 500 °C for 60 min, it crystallized as BaTiO<sub>3</sub>, for which a measurement showed a permittivity of 165.

**Claims:**

1. A method for growing oxide thin films, characterized in that the films are produced by the ALE process by using as the precursor cyclopentadienyl compounds of strontium and/or barium, together with one or more volatile titanium compounds and a reactive oxygen precursor.

2. The method according to Claim 1, characterized in that the oxide thin film to be grown is dielectric.

3. The method according to Claim 1 or 2, characterized in that there are 1-10, preferably 1-2, similar growth cycles in succession, one growth cycle being made up of the feeding of a Ba compound, Sr compound or volatile titanium compound; an inert purge; the feeding of a precursor for oxygen; and a second inert purge.

4. The method according to any of Claims 1 - 3, characterized in that the cycle ratio of the alkaline earth metal compound and the titanium compound is 0.8-1.2.

5. The method according to any of Claims 1 - 4, characterized in that the volatile titanium compound is a titanium halide, titanium alkoxide, titanium nitrate ( $\text{Ti}(\text{NO}_3)_4$ ), an alkylamino complex of titanium, a cyclopentadienyl complex of titanium, a silylamido complex of titanium, titanium dialkylthiocarbamate, or titanium- $\beta$ -diketonate.

6. The method according to any of the preceding claims, characterized in that the film growth substrate is a platinum (Pt),  $\text{RuO}_2$ ,  $\text{IrO}_2$ ,  $\text{SrRuO}_3$ ,  $\text{LaSrCoO}_3$ ,  $\text{IrO}_2/\text{Ir}$ ,  $\text{RuO}_2/\text{Pt}$ , silica ( $\text{SiO}_2$ ), silicon nitride or silicon surface.

7. The method according to any of the preceding claims, characterized in that the reactive oxygen precursor used is oxygen ( $\text{O}_2$ ), water vapor, hydrogen peroxide or an aqueous solution of hydrogen peroxide, and/or ozone.

8. The method according to any of the preceding claims, characterized in that the formula of the precursor is  $\text{M}(\text{Cp})_2$  or  $\text{M}(\text{Cp})_2\text{L}_n$ , where

- M is Sr or Ba,

- Cp is a fused or single cyclopentadienyl group of the form  $\text{Cp}^*\text{R}_m\text{H}_{5-m}$ , where
  - m is an integer 0-5 and
  - R is a hydrocarbon group, the hydrocarbon groups being mutually either the same or different,
- the Cp groups are either the same or different,
- $\text{L}_n$  is a neutral adduct ligand which binds to the metal by one or several of its atoms.

9. The method according to any of Claims 1 - 7, characterized in that

- the precursor for Sr and/or Ba is of the form  $\text{M}(\text{Cp})\text{X}$  or  $\text{M}(\text{Cp})\text{XL}_n$ , where
- M is Sr or Ba,
- Cp is a fused or single cyclopentadienyl group  $\text{Cp}^*\text{R}_m\text{H}_{5-m}$ , where
  - m is an integer 0-5 and
  - R is a hydrocarbon group, the R's being mutually either the same or different,
- X is a ligand, other than Cp, having a valence of -1 and
- L is a neutral adduct ligand which binds to the metal by one or several of its atoms.

10. The method according to Claim 8 or 9, characterized in that the cyclopentadienyl group is cyclopentadienyl, pentamethylcyclopentadienyl, triisopropylcyclopentadienyl, indenyl, or fluorenyl.

11. The method according to Claim 8 or 9, characterized in that the Cp groups are contained in the same molecule.

12. The method according to Claim 11, characterized in that the bridge between two Cp groups is made up of a substituted or unsubstituted  $\text{C}_1 - \text{C}_6$  carbon chain.

13. The method according to Claim 12, characterized in that the carbon chain forming the bridge contains a heteroatom, which is silicon, nitrogen, phosphorus, selenium, or sulfur.

14. The method according to Claim 8 or 9, characterized in that R is a substituted or unsubstituted, cyclic, linear or branched alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, amino, cyano or silyl group.

15. The method according to Claim 8 or 9, characterized in that the neutral adduct ligand L is

- (i) a hydrocarbon,
- (ii) an oxygen-containing hydrocarbon,
- (iii) a nitrogen-containing hydrocarbon,
- (iv) a sulfur-containing hydrocarbon,
- (v) a phosphorus-containing hydrocarbon,
- (vi) an arsenic-containing hydrocarbon,
- (vii) a selenium-containing hydrocarbon, and/or
- (viii) a tellurium-containing hydrocarbon.

16. The method according to Claim 8 or 9, characterized in that L is

- (a) an amine or polyamine,
- (b) a bipyridine,
- (c) a ligand depicted by the formula



(V)

in which formula G is  $-O-$ ,  $-S-$ , or  $-NR^1-$ , where  $R^1$  is hydrogen or a substituted or unsubstituted, cyclic, linear or branched, alkyl, alkenyl, aryl, alkylaryl, arylalkyl, alkoxy, thio, cyano or silyl group, and in each carbon atom of the ring according to the formula there is an  $R^1$ -like substituent, which are either mutually the same or different,

- (d) ether, or
- (e) thioether.

17. The method according to Claim 8 or 9, wherein L is an ether, polyether, amine, polyamine, bipyridine or tetrahydrofuran.

18. The method according to Claim 9, characterized in that X is a  $\beta$ -ketonate or a corresponding sulfur or nitrogen compound, alkyl, halide, amide, alkoxide, carboxylate or Schiff base.

5

19. The method according to any of the preceding claims, characterized in that the growth of the film takes place at 250-300 °C, and the postannealing carried out after the growth takes place at a temperature higher than the deposition temperature, preferably at 500 °C.

0787062-06204  
102290-290285

(57) Abstract:

The present invention relates to a method for growing oxide thin films which contain barium and/or strontium. According to the method, such thin films are made by the ALE  
5 technique by using as precursors for barium and strontium their cyclopentadienyl compounds. A thin film made by means of the invention has a high permittivity and excellent conformality.

0707062-062004

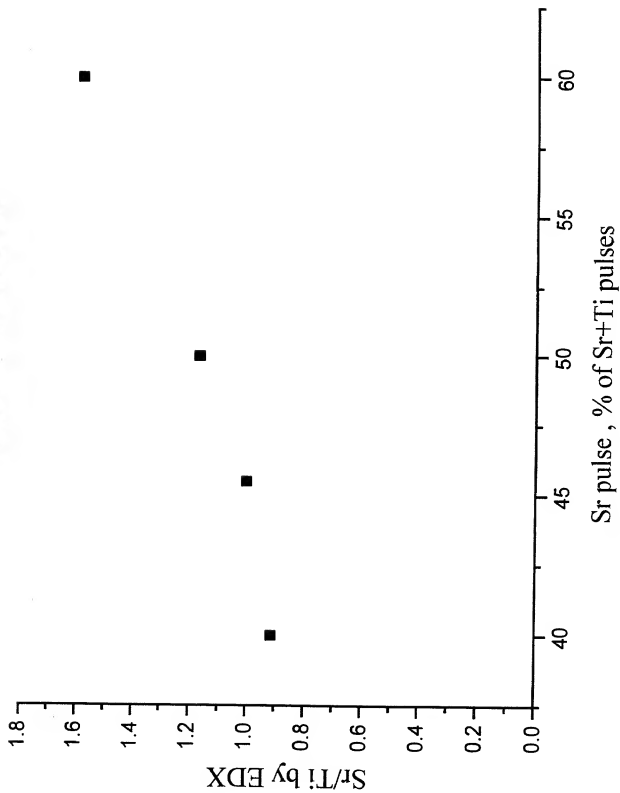


Fig. 1



108290-292860

09/787062

2/3

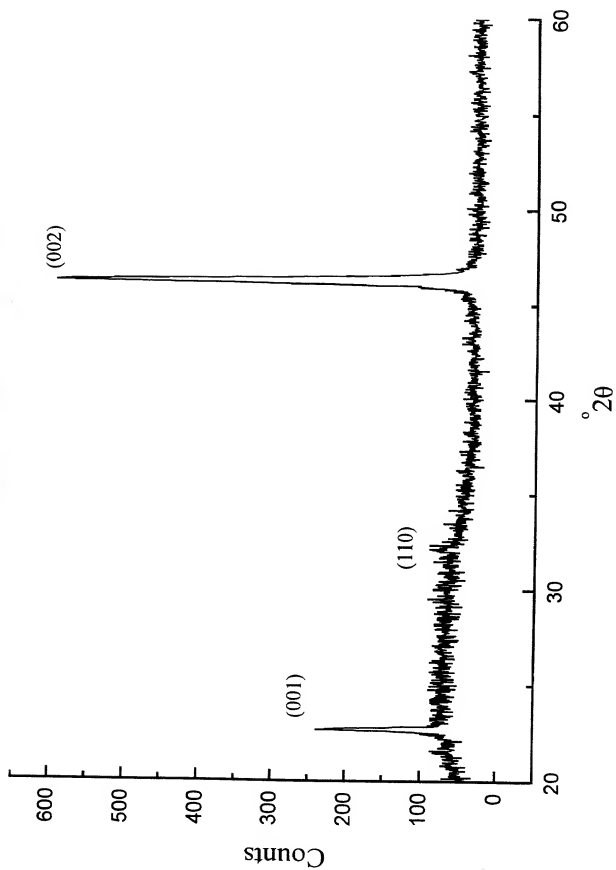


Fig. 2

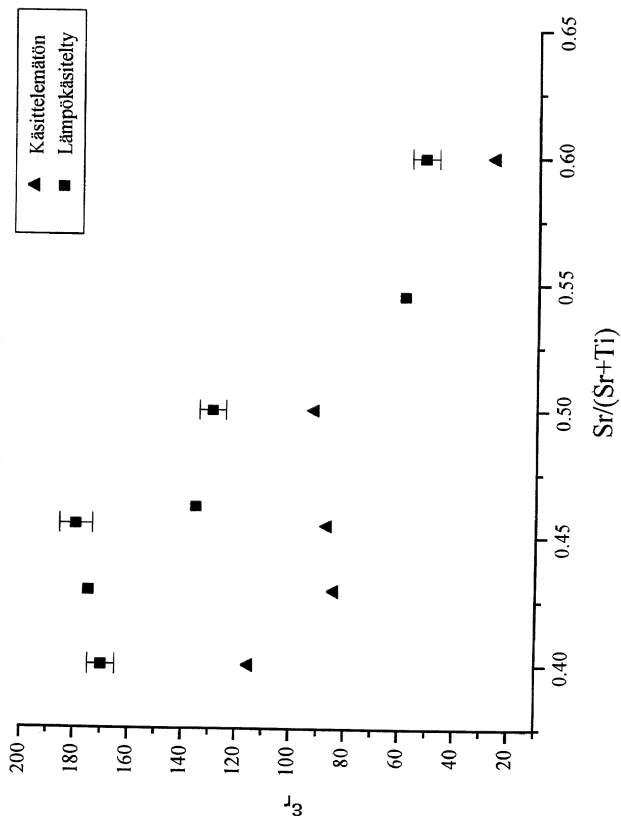


Fig. 3

**DECLARATION AND POWER OF ATTORNEY- USA PATENT APPLICATION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I believe I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled METHOD FOR GROWING OXIDE THIN FILMS CONTAINING BARIUM AND STRONTIUM; the specification of which was filed on **September 13, 1999** as Application Serial No. **09/787,062**.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above;

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56;

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

**PRIOR FOREIGN APPLICATION(S)**

Priority  
Claimed

No.: <b>FI981959</b>	Country: <b>Finland</b>	Date Filed: <b>September 11, 1998</b>	<b>Yes</b>
No.: <b>PCT/FI99/00741</b>	Country: <b>PCT</b>	Date Filed: <b>September 13, 1999</b>	<b>Yes</b>

**POWER OF ATTORNEY:** I hereby appoint the registrants of Knobbe, Martens, Olson & Bear, LLP, 620 Newport Center Drive, Sixteenth Floor, Newport Beach, California 92660, Telephone (949) 760-0404, **Customer No. 20,995**.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful, false statements may jeopardize the validity of the application or any patent issued thereon.

-----

Full name of first inventor: **Markku, LESKELÄ**

Inventor's signature *Markku Leskelä*

Date June 14, 2001

Residence: **Rauduntie 19 D, FIN-02130 Espoo, FINLAND**

Citizenship: **Finnish**

*FJX*

Post Office Address: **Rauduntie 19 D, FIN-02130 Espoo, FINLAND**

Full name of second inventor: **Mikko RITALA**

Inventor's signature *Mikko Ritala*

Date June 14, 2001

Residence: **Antreantie 8 B 4, FIN-02140 Espoo, FINLAND**

Citizenship: **Finnish**

*FJX*

Post Office Address: **Antreantie 8 B 4, FIN-02140 Espoo, FINLAND**

Full name of third inventor: **Timo HATANPÄÄ**

Inventor's signature *Timo Hatanpää*

Date June 14, 2001

Residence: **Aamuyönkuja 3 B, FIN-02210 Espoo, FINLAND**

Citizenship: **Finnish**

*FJX*

Post Office Address: **Aamuyönkuja 3 B, FIN-02210 Espoo, FINLAND**

Full name of fourth inventor: **Timo HÄNNINEN**

Inventor's signature *Timo Hänninen*

Date June 14, 2001

Residence: **Pitkäsillanranta 7 - 9 A 10, FIN-00530 Helsinki, FINLAND**

Citizenship: **Finnish**

Post Office Address: **Pitkäsillanranta 7 - 9 A 10, FIN-00530 Helsinki, FINLAND**

Full name of fifth inventor: **Marko VEHKAMÄKI**

Inventor's signature *Marko Vehkamäki*

Date June 14, 2001

Residence: **Rautalammintie 3 B 409, FIN-00550 Helsinki, FINLAND**

Citizenship: **Finnish**

Post Office Address: **Rautalammintie 3 B 409, FIN-00550 Helsinki, FINLAND**

Send Correspondence To:

**KNOBBE, MARTENS, OLSON & BEAR, LLP**

**Customer No. 20,995**